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(54) Name of Invention: Method of Manufacturing Cold
Cathode Device

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Specifications

1. Name of Invention: Method of Manufacturing Cold
Cathode
Device

2. Scope of Patent Application

In a method for manufacturing a cold cathode device having projecting cathodes that protrude from a semiconductor surface and a gate electrode with electrode holes encircling the said projecting cathodes, a method of manufacturing a cold cathode device which is characterized by having --

A process for forming a photoresist on a silicon substrate's prescribed region so as to form the above-noted projecting cathodes,

A process for implanting an impurity from the upper layer of the above-noted substrate,

A process for mixing in the impurity from the surface of the above-noted substrate,

A process for causing anodic oxidation of the above-noted substrate surface to form an oxide film,

A process for creating a first metallic coating on the above-noted substrate surface,

A process for removing the above-noted photoresist,

A process using the above-noted first metallic coating as a mask in doing etching so as to remove the part of the above-noted oxide film situated under the above-noted photoresist, thus exposing the still unoxidized part of the above-noted substrate and so to form projecting parts united with the above-noted substrate, and

A process that applies a coating of a second metal--which may even be a metal identical to the first coat--to the surface of the above-noted projecting parts, so forming the above-noted projecting cathodes.

3. Detailed Explanation of Invention

Field for Commercial Utilization: This invention is one bearing on a method for manufacturing cold cathode devices useable in such things as picture elements in display devices.

Usual Technology: Figure 2 is a cross-sectional diagram illustrating the usual cold cathode described in the *Journal of Applied Physics*, 47[12] (1978-12), American Institute of Physics, C.A. Spindt, "Physical properties of thin-film field emission cathodes with molybdenum cones," pp. 5248- 5263. The above cold cathode is made up of SiO_2 , dielectric film 22 on silicon substrate 21, and of projecting conical cathodes 23 in hollow spaces 22a of

dielectric film 22. Also, gate electrodes 24 are installed to have an electrode hole 24a in dielectric film 22 and surround the projecting tips of electrodes 23. Above-noted projecting cathodes 23 and gate electrodes 24 are made of molybdenum. Projecting cathodes 23 in particular are made entirely of molybdenum.

Figures 3(a) through 3(e) are diagrams illustrating the fabrication processes of the above-noted usual cold cathodes.

First, as shown in Fig. 3(a), the surface of silicon substrate 31 is oxidized, forming dielectric film 32 of SiO_2 ; and molybdenum is sputtered on it to form Mo film 33. Here, as described by the above-noted publication, the above-noted silicon substrate's volume resistance rate is 0.01SCcm. Next, a photoresist is applied on Mo film 33 and patterned by electron-beam exposure to form photoresist pattern 34.

Then, as shown in Fig. 3(a), photoresist 34 is left in place while Mo film 33 is selectively etched to form hole 33a.

Next, the above-noted resist film is removed and dielectric film 32 is etched with fluoric acid (an aqueous solution of hydrogen fluoride). Conditions following the etching are shown in Fig. 3(c). At this time, the silicon oxide is corroded by the fluoric acid, but silicon is not, so that a part of dielectric film 32 is removed to form hollow 32a in which silicon substrate 31 is exposed. Moreover, as the molybdenum is not corroded by the fluoric acid, the above-noted hollow 32a widens out as far as the lower part of Mo film 33; and Mo film 33 is shaped as a film with a prescribed undercut.

Now, while rotating silicon substrate 31 horizontally (parallel to the surface of silicon substrate 31) on the axis of hollow 32a's center, aluminum is vapor-deposited onto Mo film 33 at a slant from above Mo film 33, for instance from a direction above Mo film 33 at angle N to form the aluminum film 35 of Figure 3(d). This process forms aluminum film 35 at edge 33b of molybdenum film 33 on silicon substrate 31 at an angle to the vertical of substrate 31. Also, as needed, the diameter of hole 33a can be made smaller by the above vapor-deposition of aluminum.

Next, through hole 33a created by the above-described

aluminum vapor-deposition at a slant to the vertical of substrate 31, one can form conical projecting cathode 36, as shown in Fig. 3(e), by vapor-depositing Mo on the exposed part of silicon substrate 31 in hollow 32a.

Finally, removing aluminum film 35 yields the cold cathode shown in Figure 2.

According to the description in the above-noted publication, the cold cathode formed by the above-described fabrication method has a curve diameter in the projecting cathode which is small, making it possible to have a short distance between the gate electrode and the projecting cathode. So, one can get a powerful field strength.

Problems the Invention Seeks to Resolve Nevertheless, in the above-noted usual method of manufacture, because positioning the silicon substrate's axis of rotation has been difficult in vapor-depositing the aluminum, the problem has existed that it is difficult to create the projecting cathode in a prescribed position. Also, the above-noted usual manufacturing method has the problem that its processes are complex due to forming many cold cathodes on a substrate with a large area.

So, we devised this invention to resolve the above-noted problems with the usual techniques; and we assigned it the goal of providing an improved method of manufacturing a cold cathode device.

Means to Resolve the Problems: In a method for fabricating cold cathode devices with projecting cathodes that protrude from a semiconductor surface and a gate electrode with electrode holes encircling the said projecting cathodes, a method of manufacturing a cold cathode device which is characterized by having --

A process that forms a photoresist on the region of a silicon substrate prescribed for forming the above-noted projecting cathodes,

A process that implants an impurity from the surface of the above-noted substrate,

A process that admixes the impurity from the upper layer of the above-noted substrate,

A process that does anodic oxidation of the above-noted substrate surface to form an oxide film,

A process that forms a first metallic coating on the above-noted substrate surface,

A process to remove the above-noted photoresist,

A process using the above-noted first metallic coating as a mask to etch away the part of the above-noted oxide film located under the above-noted photoresist, thus exposing the unoxidized part of the above-noted substrate to form projecting parts joined to the above-noted substrate, and

A process applying a coating of a second metal--which may even be a metal identical to the first coat--to the surface of the above-noted projecting parts, thus forming the above-noted projecting cathodes.

Effects: When implanting the impurity into the substrate with this invention's manufacturing method, the impurity goes around to the photoresist's under side; but the impurity concentration is lower the nearer it is to the center under the photoresist and the deeper it is. Next, in doing anodic oxidation, the oxidation will proceed more quickly in the parts where the impurity concentration is highest. So, a conical unoxidized area will be formed under the photoresist.

Next, when the resist is removed after applying the above-noted first metallic coating, the above-noted first metal will have a structure with a hole right over the above-noted unoxidized conical part. Then when the oxide film is etched with this first metal as a mask, the etching will proceed from near the above-noted hole, removing oxide film from below the above-noted opening and leaving the unoxidized part in the above-noted conical form. Then a second metal coating is formed on the above-noted conical unoxidized part. This second metal film has a stable surface work function and impulse traits against ions, so that protruding cathodes are obtained that have desirable traits.

The above-noted photoresist is used also in forming gate electrodes. Since the area where the said photoresist was will become electrode holes, the relative positional relationship of the electrode holes to the cathode tips are determined by a self-alignment method.

Application Example

In the following, we will explain this invention based on the figures of application examples.

Figures 1(a) through (f) are outline cross-sectional dia-

grams showing the manufacturing processes for cold cathodes from this invention. To explain the makeup of this application example based on Fig. 1(f): Substrate 1 is a monocrystalline silicon wafer, an alumina substrate or an amorphous silicon layer laminated on plate glass. The above-noted substrate 1 has conical projections with sharp tips; and the above-noted projections 1a are formed so as to be located in the center of hollows 2a in SiO_2 dielectric film 2 and formed on above-noted substrate 1.

Also, on above-noted projections 1a is formed metallic film 3, with projections 1a and metallic film 3 constituting the projecting cathodes 10. Gate electrode 4 is installed on above-noted dielectric film 2 and has electrode holes 4 which surround the tip areas of projecting cathodes 10. Projecting cathodes 10 are at the center of electrode holes 4a. In this application example the above-noted gate electrodes may be made up with two kinds of metal coated onto them. In the above-noted makeup, when tens or hundreds of volts are impressed between the projecting cathodes 10 and gate electrodes to create a strong field of some 10^7V/cm , ions will be emitted from the surface, and especially from the tips of projecting cathodes 10.

We now will explain the above-noted method for cold cathode fabrication, following Figures 1(a) through (f).

First, as shown in Figure 1(a), photoresist 42 is applied on substrate 1 and a pattern is created. For the above-noted substrate, a monocrystalline silicon wafer, or either an alumina substrate or amorphous silicon laminated on plate glass can be used. Above-noted photoresist 42 is formed by photolithography into circles some 2Fm in diameter.

Next, ion dispersion or implantation is done from the top layer of substrate 1. This implantation is done to create a prescribed concentration gradient. The above-noted concentration gradient becomes lower as it goes deeper into substrate 1's surface layer and as it approaches the area right under photoresist 42 or as it goes deeper under it.

Figure 1(a)'s dotted lines 43, 44 and 45 are curves for the equal concentrations of the above-noted impurity formed in substrate 1 and respectively indicate $1\text{H}10^{-17} \text{ions/cm}^3$, $1\text{H}10^{-18} \text{ion/cm}^3$ and $1\text{H}10^{-19} \text{ion/cm}^3$.*

Again, it is desirable that the above-noted impurity form a p-type substrate; and ordinarily boron is used. By forming a p-type substrate, one can reduce the effects of voltage drops due to potential barriers at the interface of the silicon and silicon oxide.

Next, one forms the oxide layer (SiO_2 film) by anodic oxidation of the surface layer of substrate 1 with the impurity implanted by the above-described process. Anodic oxidation is done by electrolysis, immersing above-noted substrate 1 (the anode) and platinum (the cathode).

The oxidation rate during the above-noted anodic oxidation is affected by the impurity concentration in the silicon, with the oxidation rate being greater the higher the impurity concentration. Hence, the surface of the oxide film in the oxidation process will roughly match the impurity's equal-concentration curve. As described above, the impurity's concentration gradient directly under photoresist 42 will be lower the closer it is to the center; and the

* [Powers of 10 here did not fax well and may be -11, -12 and -13. Translator].

deeper it is the lower it will be. So, by doing the above-noted anodic oxidation, the round portion remains without being oxidized.

With the above-described process, dielectric film 2 (SiO_2 film) will be formed as shown in Fig.(b) on the top surface of substrate 1. The area near the interface of substrate 1's silicon and SiO_2 layer 2 acts as a cathode in the above-noted process since it contains implanted impurity.

The electrolytic solution used for the above-noted anodic oxidation may be any generally known electrolyte such as solutions of ethylene glycol and n-methylacetamide; and we can mention solutions to which such salts as potassium nitrate or ammonium nitrate are added. The above-noted anodic oxidation can be done by either the constant current method or the constant voltage method.

In the above-noted anodic oxidation process, photoresist 42 is kept in the same situation, so that after finishing the anodic oxidation it will be on silicon oxide film 2.

Next, as shown in Fig. 1(c), metallic layer 47, which is to be a gate electrode, is formed on SiO_2 film 2. For the above-noted metal, one could use, for instance, molybdenum, etc. The above-noted metallic layer usually is formed by vapor deposition.

Since at this time photoresist 42, as described above, is in its original position, metallic layer 47 will be formed in part on the said photoresist.

Then, removing photoresist 42 will simultaneously remove part of metallic layer 47 (by the lift-off method). As a result, metallic film 47 remaining on silicon oxide film 2 will form gate electrode 4, and electrode holes 4a will be formed where the photoresist was.

In the above-noted method, the relative positional relationships between electrode holes 4a and conical protrusions 1a are maintained by self-alignment, with the protrusions situated just below electrode holes 4a [Fig. 1(d)].

Next, one etches SiO_2 film 2. This etching is usually done with three stipulated fluoride acids. By using fluoric acids at the above-noted concentration, only the silicon oxide will be etched, and the silicon and gate electrode 4 will remain. Also, by controlling the etching time, hollow 2a will be formed (undercut) as far as the lower part of the gate electrode, as shown in Fig. 1(e), with protrusion 1a formed in the center of hollow 2a.

Finally, coating a metal on above-noted protrusion 1a creates metallic film 3 shown in Fig. 1(f). Protruding cathode 10 is made of the above-noted protrusions 1a and metal film 3. It is desirable that the above-noted metallic film 3 be formed with a depth in the range of 100~3000D. For the above-noted metallic film, metals are used such as molybdenum or tungsten which have a stable surface work function suited to high-field electron emitting traits and resistance to ion impulses.

With the above steps the cold cathode device is completed. By the same method multiple cold cathodes can be formed simultaneously on the same silicon substrate.

Effectiveness of Invention: As explained above, with this

invention's manufacturing method one forms protrusions from the substrate itself so that the usual method's processes of vapor-depositing aluminum film at an angle and removing the aluminum film become unnecessary. Also, because with this invention's manufacturing method one can form protruding electrodes in areas directly under the photoresists and form electrode holes where the photoresist was, the locations of the protruding electrodes and electrode holes can be fixed by the self-alignment method. Consequently, the fabricating process can be simplified.

Furthermore, with this invention's manufacturing method multiple cold cathodes can be formed simultaneously on a large-area substrate.

Again, with this invention's cold cathodes obtained by the above-described manufacturing method the shape of these protruding cathodes is determined by the photoresists and the concentration gradient of the impurity, so that even when forming multiple cold cathodes simultaneously one can get protruding cathodes whose shape is uniform.

4. Simple Explanation of Figures

Figures 1(a) through (f) are outline cross-sectional diagrams showing the fabrication processes of one example of applying this invention.

Figure 2 is a cross-sectional outline diagram of the usual cold cathode device.

Figures 3(a) through (e) are cross-sectional diagrams illustrating the fabricating processes for the usual cold cathode device.

[Keying symbols]

- 1, 21, 31 Substrates
- 1a Projecting part
- 2, 22, 32 Dielectric films
- 2a, 22a, 32a ... Hollow parts
- 3 Metallic film
- 4, 24, 34 Gate electrodes
- 4a, 24a, 34a ... Electrode holes
- 10, 23, 36 Protruding cathodes
- 42 Photoresist

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